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DESCRIPTION

Composite of Aluminum Alloy and Resin Composition and
Production Method Therefor

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Technical Field:

The present invention relates to a composite of an aluminum alloy and a resin composition for use in housings of electronic devices, housings of home electrical devices, structural parts, mechanical parts, etc., and also relates to a production method therefor. More particularly, the present invention relates to a structure having a high-strength thermoplastic resin composition integrated with a shaped aluminum alloy material produced by various machining process. That is, the present invention relates to an aluminum alloy-and-resin composition composite for use in various electronic devices for mobile applications, home electrical products, medical devices, structural parts for vehicles, vehicle-mounted products, construction material parts, structural parts of other equipment, parts for exterior applications, and so forth, and also relates to a production method therefor.

Background Art:

Techniques for firmly integrating a metal and a resin with each other are demanded in a wide variety of fields such as those of manufacturing parts of automobiles, home electrical products, industrial equipment, etc. For

this purpose, many adhesives have been developed. Among the proposed adhesives include very excellent ones. Adhesives that exhibit their function at ordinary temperature or upon heating are used for bonding to
5 integrate a metal and a synthetic resin with each other. The method using such an adhesive is now a common technique.

However, the present inventors presumed that there is an even more rational bonding method, regardless of
10 whether or not an adhesive is used, and conducted exhaustive studies and development to find such a bonding method. Our object was to integrate a high-strength engineering resin with metals, such as magnesium, aluminum, alloys of these metals, stainless steel and other iron
15 alloys, so firmly that the resulting integrated article would permanently maintain the strength at a practical level. In the present state of the art, bonding a metal and a shaped resin material together by using an adhesive is a processing step that is commonly carried out in the
20 industrial fields of home electrical devices, machinery, everyday items, and so forth. However, consideration is not given much to the matching of linear expansion coefficient between the metal and the resin when selecting constituent materials therefor.

25 In the actual circumstances, elasticity is imparted to the adhesive so that the adhesive layer serves to relax internal strains due to a linear expansion coefficient difference between the metal and resin materials, thereby

maintaining the bonded condition. This is a kind of deception in the sense that the distortional stress remains in the adhesive layer. Thus, the conventional technique is not 100 percent satisfactory in view of the
5 fundamental idea of integrating together the metal and the resin permanently. The reason why no particular question has been raised about this situation is deemed as follows.

That is, adhesives are developed in the technical field of adhesives. Their goal is to develop universal and
10 durable adhesives. Therefore, we infer that developers in the technical field of adhesives usually do not consider to develop a metal treating method by conceiving a fine structure of the metal surface that is suitable for bonding, or to improve the resin composition to thereby
15 form a product having a coefficient of linear expansion equal to that of the metal.

It is inferred that adhesive developers deem that the above-described development and design belong to the fields of metal working and resin manufactures, or they
20 consider that their mission is to diligently develop elastic adhesives, in which they specialize, although it is technically difficult to develop such adhesives. In short, fundamental examination of constituent materials of both the metal and the resin composition to be bonded to
25 each other has not heretofore been made among persons skilled in these technical fields.

Meanwhile, the present inventors conducted exhaustive studies and development and found that bond

strength increases uniquely if a shaped aluminum material is dipped in an aqueous solution of at least one selected from the group consisting of ammonia, hydrazine, and a water-soluble amine compound and thereafter brought into
5 contact with a thermoplastic resin composition containing polybutylene terephthalate (hereinafter referred to as "PBT") as a main component under ordinary injection molding temperature and pressure conditions (we proposed this finding as WO 03/064150 A1).

10 It has also heretofore been known that a metal-and-resin composite product is formed by insert-molding a metal product [for example, see Japanese Patent Application Unexamined Publication (KOKAI) Nos. 2001-225352, Sho 54-13588, Sho 54-13587, Sho 58-217679, Sho 50-
15 158539, and Hei 5-70969]. However, these conventional composite producing methods are for producing electric contacts, aluminum foil, etc., and hence cannot provide firm bonding adequate for mechanical structures that are required to exhibit strong bond strength (adhesion) and
20 rigidity.

The present inventors further carried out exhaustive researches and development from the viewpoint of finding substances suitable for use as a metal material and a resin material. In this regard, however, both metal and
25 resin materials should not be very special in order to be usable in practical application. In order^a for a thermoplastic resin composition to bond to a metal permanently, the linear expansion coefficient thereof

needs to be matched to that of the metal.

The present inventors selected as a resin composition a polybutylene terephthalate resin (hereinafter referred to as "PBT") exhibiting satisfactory
5 heat resistance and strength and having low hygroscopicity and moderate chemical resistance. The linear expansion coefficients of thermoplastic resins are much higher than those of metals. PBT has a linear expansion coefficient of 8 to $10 \times 10^{-5}^{\circ}\text{C}^{-1}$, which is much higher than those of
10 metals, which are about 1.0 to $2.5 \times 10^{-5}^{\circ}\text{C}^{-1}$. Among metals, aluminum is one of those having the highest linear expansion coefficients. The linear expansion coefficient of an aluminum alloy containing pure aluminum is 2.2 to $2.5 \times 10^{-5}^{\circ}\text{C}^{-1}$. Therefore, we selected as a metal an
15 aluminum alloy that has a high coefficient of linear expansion and hence allows the numeral range thereof to be easily matched to that of the resin composition and that enables various physical properties to be obtained by alloying.

20 First, PBT was compounded with a large amount of fibrous filler, etc., and another polymer was added thereto to form a thermoplastic resin composition. In this way, we attempted to make the linear expansion coefficient of the thermoplastic resin composition coincident with
25 that of the aluminum alloy. We prepared various compounds and formed rectangular molded articles by injection molding. Coefficients of linear expansion in the lengthwise direction (direction of the resin flow during

molding) and in the crosswise direction were measured to prepare a large number of pieces of data. By analyzing the data, we found a thermoplastic resin composition having a linear expansion coefficient approximately equal to that
5 of the aluminum alloy.

Regarding aluminum alloys, a surface treatment method preferable for bonding of them has been developed from old times. We examined usability of this surface treatment method. Aluminum alloys containing copper that
10 are standardized as "2000 series" by Japanese Industrial Standards (JIS), also known as "duralumin", are mostly used for aircraft. For the "2000 series" aluminum alloys, treatment methods for obtaining long-term stability in severe service environments have been developed, although
15 these are concerned with the bonding of one aluminum alloy to another. For example, the EPL etching method shown in D2651 of ASTM (American Society of Testing and Materials) is a process in which duralumin is washed with an alkaline aqueous solution and thereafter dipped in concentrated
20 sulfuric acid containing chromium, followed by washing with ion-exchange water.

The duralumin treated by this method is covered at the surface thereof with fine recesses having a diameter of about 0.04 μm and with small whisker projections
25 extending vertically from the openings of the fine recesses. The thickness of the thinnest film portion of the aluminum oxide layer covering the metallic aluminum is said to be about 5 nm. The treated duralumin strengthens

the interlocking with the adhesive by the surface where
recesses and projections coexist with each other. ASTM
D3933 shows a method wherein an aluminum alloy is anodized
in an aqueous phosphoric acid solution. On the surface of
5 the aluminum alloy treated by this method also, deep pores
(depth of 0.1 to 0.3 μm) having a diameter of 0.04 μm and
short whiskers extending vertically from the openings of
the pores are observed.

The thickness of the thinnest film portion of the
10 aluminum oxide layer covering the metallic aluminum is
considered to be several nanometers. It should be noted,
however, that these methods may be said to be special
methods for manufacturing structural materials for
aircraft. Because they use a large amount of ion-exchange
15 water, the treatment methods are difficult to adopt for
use in ordinary liquid treatment lines, i.e. plating
equipment, aluminum anodizing equipment, equipment for
caustic treatment of magnesium alloy, etc.

Meanwhile, the document of Int. J, Adhes. 5(1), 40-
20 42 (1985), D. J. Arrowsmith and A. W. Clifford states that
an aluminum alloy having high durability and good adhesion
can be obtained simply by dip-etching in an aqueous
solution of at least 15% caustic soda, for several minutes,
followed by thorough rinsing with water. This report does
25 not assume that the treated aluminum alloy will be used
for aircraft. The treatment is deemed to be effective in
its own way in terms of adhesion because recesses and
projections are formed on the surface to some extent by

the method. However, as compared, at least, with the complicated methods described above, it is inferred that the surface area is small and the anchor effect (bonding effect) is low even if the treated surface has a certain
5 degree of roughness.

On the other hand, the thinnest film portion of the aluminum oxide layer covering the metallic aluminum part also must be thin. However, this gives rise to no practical problem because long-term stability is needed
10 regardless of whether the aluminum alloy is used for aircraft or not. In short, there is the question as to the extent to which the surface area of the aluminum alloy needs to be increased in order to obtain the required anchor effect. For example, there is the view that an
15 excessively finely-etched surface may prevent the resin or the adhesive from sufficiently entering (filling) the pores and recesses formed on the treated surface, resulting in the finely etching process being practically worthless.

20 Regarding the thickness of the aluminum oxide layer, we are interested in the thickness of the thinnest film portion that is required to ensure satisfactory durability, and also interested in whether or not durability is actually determined only by the thickness of the thinnest
25 film portion. Therefore, the present inventors first carried out aluminum alloy treatment by the above-described simple caustic soda dipping method (hereinafter referred to as "treatment ①") using the aluminum A5052

alloy (JIS), which is considered to be used for the largest number of applications. Next, we performed various bonding tests by using an aluminum alloy having been subjected to aluminum anodizing treatment to a halfway point in the process (hereinafter referred to as "treatment ②"), assuming a method close to those specified in ASTM D2651 and D3933.

Incidentally, the aluminum anodizing treatment is usually carried out in the following sequence: degreasing of the aluminum alloy; alkali etching; polishing (acid etching); anodizing; dyeing; and sealing. The aluminum surface immediately after the anodizing process has the largest surface area. The anodized aluminum surface is closely crowded with cylindrical crystals of aluminum oxide having pores with a diameter of 0.05 to 0.08 μm and a depth reaching several to 20 μm . Thus, the cylindrical crystals form a surface that is crowded with an infinite number of openings.

The pore diameter of the aluminum oxide is slightly larger and the pore length is much longer than in the case of duralumin treated by ASTM D3933. The thickness of the aluminum oxide at the pore bottom, that is, the thickness of the thinnest film portion of the aluminum oxide layer covering the metallic aluminum seems to be about 1 nm or more. However, the precise thickness of the thinnest film portion is not clear.

The present inventors performed various experiments by using test pieces of an aluminum alloy treated by two

different processes, i.e. treatment ① and treatment ②, and also using a PBT resin having a coefficient of linear expansion adjusted to the same level as that of the aluminum alloy. We expected that if the aluminum alloy and the resin were integrated together whichever method we used, interesting features would appear in the strength of the integrated article. Speaking plainly, the results were as follows. With the treatment ①, satisfactory strength could not be obtained for some integrated articles. Therefore, we found it necessary to further scheme to solve the problem. With the treatment ②, bonding using an adhesive showed excellent results. With other pore forming methods, however, results were worse than those with the treatment ①, which is a simple and easy method. Thus, we found it impossible to predict results only with the size of the surface area. Therefore, the present inventors decided to assume a favorable aluminum alloy surface configuration and to establish an aluminum surface configuration that allows a resin composition and an aluminum alloy to be integrated together excellently.

With the above-described technical background, the present invention was made to attain the following objects.

An object of the present invention is to obtain an aluminum alloy-and-resin composite wherein a thermoplastic resin composition and a shaped aluminum alloy material are made to adhere to each other so strongly that they will not readily separate from each other by treating the aluminum alloy surface, and also obtain a production

method therefor.

Another object of the present invention is to obtain an aluminum alloy-and-resin composite capable of making housings and parts of various devices, structures, etc.
5 free from problems in terms of configuration, structure and mechanical strength, and also obtain a production method therefor.

Still another object of the present invention is to obtain an aluminum alloy-and-resin composite useful for
10 reducing the weight of housings and parts of electronic devices, structures, etc. and for simplifying device manufacturing processes, and also obtain a production method therefor.

15 Disclosure of the Invention:

An aluminum alloy-and-resin composition composite according to a first feature of the present invention comprises a shaped aluminum alloy material having a surface with a surface roughness of 5 μm to 50 μm and
20 having fine recesses or projections of not larger than 1 μm on the surface. The aluminum alloy-and-resin composition composite further comprises a thermoplastic resin composition fixed to the surface of the shaped aluminum alloy material by entering the recesses or
25 engaging the projections. The thermoplastic resin composition contains as a main component a polybutylene terephthalate resin or polyphenylene sulfide having an average coefficient of lengthwise and crosswise linear

expansion of $2 \text{ to } 4 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$.

An aluminum alloy-and-resin composition composite according to a second feature of the present invention comprises a shaped aluminum alloy material having a
5 surface with a surface roughness of $1 \text{ } \mu\text{m}$ to $10 \text{ } \mu\text{m}$ and having fine recesses or projections of $0.01 \text{ } \mu\text{m}$ to $0.1 \text{ } \mu\text{m}$ in diameter on the surface. The surface of the shaped aluminum alloy material is covered with a + trivalent aluminum compound having an average thickness of about
10 $0.001 \text{ } \mu\text{m}$. The aluminum alloy-and-resin composition composite further comprises a thermoplastic resin composition fixed to the surface of the shaped aluminum alloy material by entering the recesses or engaging the projections. The thermoplastic resin composition contains
15 as a main component a polybutylene terephthalate resin or polyphenylene sulfide having an average coefficient of lengthwise and crosswise linear expansion of 2 to
 $4 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$.

An aluminum alloy-and-resin composition composite
20 according to a third feature of the present invention is characterized as follows. In the aluminum alloy-and-resin composition composite according to the first or second feature of the present invention, the recesses or the projections include first recesses or first projections
25 having a first diameter of $0.03 \text{ } \mu\text{m}$ to $0.1 \text{ } \mu\text{m}$ and a depth about equal to or larger than the first diameter. The number of first recesses or first projections per $1 \text{ } \mu\text{m}$ square area of the surface is not less than 10. The

recesses or the projections further include second recesses or second projections having a second diameter of 0.01 μm to 0.03 μm and a depth about equal to or larger than the second diameter. The number of second recesses or
5 second projections per 1 μm square area of the surface is not less than 50.

An aluminum alloy-and-resin composition composite according to a fourth feature of the present invention is characterized as follows. In the aluminum alloy-and-resin
10 composition composite according to one feature selected from the first to third features of the present invention, the thermoplastic resin composition is fixed to the surface of the shaped aluminum alloy material by bonding using an adhesive.

15 An aluminum alloy-and-resin composition composite according to a fifth feature of the present invention is characterized as follows. In the aluminum alloy-and-resin composition composite according to one feature selected from the first to third features of the present invention,
20 the thermoplastic resin composition is fixed to the surface of the shaped aluminum alloy material by injection molding, heat pressing, or co-extrusion.

According to a sixth feature thereof, the present invention provides a production method for the aluminum
25 alloy-and-resin composition composite according to one feature selected from the first to third features of the present invention. The production method is characterized as follows.

A coated shaped aluminum alloy material having a thin polyalkylene terephthalate film or polyphenylene sulfide adhering to a surface thereof is produced from the above-described shaped aluminum alloy material and an
5 organic solvent solution of a polyalkylene terephthalate resin or polyphenylene sulfide. The coated shaped aluminum alloy material is inserted into an injection mold. Then, the above-described polyalkylene terephthalate resin or polyphenylene sulfide is injected into the injection mold.

10 According to a seventh feature thereof, the present invention provides a production method for the aluminum alloy-and-resin composition composite according to one feature selected from the first to third features of the present invention. The production method is characterized
15 as follows.

The above-described shaped aluminum alloy material is coated with a urethane curable or epoxy curable paint or ink. After the paint or ink has been hardened, the coated shaped aluminum alloy material is inserted into an
20 injection mold. Then, the above-described polyalkylene terephthalate resin or polyphenylene sulfide is injected into the injection mold.

According to an eighth feature thereof, the present invention provides a production method for the aluminum
25 alloy-and-resin composition composite according to one feature selected from the first to third features of the present invention. The production method is characterized as follows.

The above-described shaped aluminum alloy material is heated to not lower than 200°C, and the above-described polyalkylene terephthalate resin or polyphenylene sulfide is melted and brought into contact with the shaped
5 aluminum alloy material under pressure.

According to a ninth feature thereof, the present invention provides a production method for the aluminum alloy-and-resin composition composite according to one feature selected from the first to third features of the
10 present invention. The production method is characterized as follows.

The above-described shaped aluminum alloy material is dipped in an aqueous solution of at least one selected from the group consisting of hydrazine, ammonia, and an
15 amine compound. The dipped shaped aluminum alloy material is inserted into an injection mold. Then, the above-described polyalkylene terephthalate resin or polyphenylene sulfide is injected into the injection mold.

The composite of an aluminum alloy and a resin
20 composition and the production method therefor according to the present invention will be described below in detail for each of the above-described elements.

[Shaped Aluminum Alloy Material]

As the aluminum alloy, it is possible to use various
25 aluminum alloys such as those standardized as "1000 series" to "7000 series" by JIS (Japanese Industrial Standards) and those of die-casting grade. First, the aluminum alloy is formed by various machining process into

a configuration necessary for use as an insert in injection molding process to prepare a shaped aluminum alloy material as one of a pair of materials to be bonded together ("fixing" is occasionally used as a synonym for
5 "bonding" in the present invention,). The shaped metal material processed into a necessary configuration and structure requires that the surface thereof that is to be bonded should not be oxidized thick and should be free from oil matter or an oxide of oil matter that may be
10 attached to the surface during machining. When it is clear that rust is present on the surface of the shaped aluminum alloy material as a result of it having been allowed to stand for a long period of time, the rust needs to be removed by polishing or the like. It is also preferable to
15 carry out dry or wet blasting immediately before the process described below. The dry or wet blasting process may serve also as polishing.

[Pretreatment Process: Cleaning and Etching]

The shaped metal material is subjected to degreasing
20 and cleaning to remove machining oil or other contamination from the surface thereof. For degreasing, commercially available metal degreasing agents are usable, and it is particularly preferable to use them when mass-production is made. As a simple and easy method, the
25 shaped aluminum alloy material should preferably be dipped in a water-soluble organic solvent, e.g. acetone, ethanol, or isopropyl alcohol. To perform cleaning even more thoroughly, the shaped aluminum alloy material should

preferably be dip-treated, as stated above, under application of ultrasonic waves. In either case, the shaped aluminum alloy material is rinsed with water after the degreasing process.

5 After these processes, the shaped aluminum alloy material is dipped in a 1 to 10% aqueous caustic soda solution for from several tens of seconds to several minutes, followed by rinsing with water. In the present invention, this process is referred to as "alkali etching".
10 By this process, the aluminum oxide and aluminum hydroxide layer covering the aluminum alloy surface is dissolved. Further, the inside metallic aluminum also dissolves while releasing hydrogen. As a result, the aluminum alloy surface is roughened to a surface roughness of 5 to 50 μm
15 even if it is flat before the treatment.

The surface layer becomes a thin oxidized aluminum layer. It is stated in a document that + trivalent aluminum atoms form $\text{AlO}(\text{OH})$ as a main structure. At this stage, even if the aluminum surface is analyzed at a
20 deepened angle by X-ray photoelectron spectroscopy (XPS), only a few metallic aluminum atoms can be detected. XPS is said to be capable of analyzing the aluminum alloy to a depth of about 1 nm from the surface thereof. Therefore, the thickness of the aluminum oxide film is considered to
25 be 1 to 2 nm. Incidentally, in the XPS analysis of aluminum alloys not subjected to alkali etching, that is, aluminum alloys (A5052 and A1100) subjected to only degreasing and rinsing, zero-valent aluminum can be

clearly detected with a sensitivity of about 1/2 to 1/3 of that for + trivalent aluminum. Therefore, it can be presumed that the ordinary aluminum alloys are covered with an aluminum oxide film of about 0.5 to 1.0 nm in
5 thickness. In short, the oxide film thickness can be surely increased only by etching with caustic soda.

[Fine Etching]

The alkali etching as pretreatment process enables large recesses or projections to be formed on the aluminum
10 surface and allows the thickness of the aluminum oxide film on the surface to be increased. The purpose of this process is to form even finer recesses or projections on the aluminum surface. Experiments performed by the present inventors revealed that the hydroxide ion concentration is
15 important. The object of this process was almost attained by dipping the aluminum alloy in an aqueous solution of at least one of caustic soda, soda aluminate, soda pyrophosphate, ammonia, hydrazine, and methylamine, which had been adjusted to pH 10.0 to 11.5.

20 For example, several hundred cc of an aqueous ammonia solution containing an ammonia concentration of several percent and several hundred cc of an aqueous caustic soda solution diluted to a caustic soda concentration of not more than 1% are prepared. A pH meter
25 is put into the aqueous ammonia solution. While the aqueous ammonia solution is being stirred, the aqueous caustic soda solution is dropped into the aqueous ammonia solution to adjust the pH in the neighborhood of 11.0. The

aluminum alloy having completed the pretreatment process is dipped in the aqueous solution for from several minutes to several tens of minutes, followed by rinsing with water.

The dipping in the low base concentration aqueous
5 solution causes the aluminum to dissolve while releasing hydrogen, although the rate of etching is low. As a result, fine recesses having a very small diameter are formed. Repeating the aluminum alloy treatment causes the pH to lower. Therefore, caustic soda may be added so that the pH
10 is kept in the range of 10.0 to 11.5. Temperature and time are also important factors. Dipping at a higher temperature for a longer period of time causes the recess diameter to be undesirably increased as in the case of the foregoing alkali etching.

15 Dipping for several minutes at a temperature in the neighborhood of room temperature is preferable. Such a dipping process produces fine recesses of about 0.01 to 0.1 μm in diameter. The density of such recesses is as follows. The number of recesses having a diameter of 0.01
20 to 0.03 μm per 1 μm square area of the surface is from 50 to 500. The number of recesses having a diameter of 0.03 to 0.1 μm per 1 μm square area of the surface is from 10 to 50. When the aluminum alloy surface is analyzed by XPS,
25 only a very small quantity of zero-valent aluminum can be detected. Most of the detected aluminum is + trivalent aluminum. This fact shows that the aluminum alloy surface is covered with a + trivalent aluminum compound having a thickness of about 1 nm (0.001 μm), if we must say, from 1

to 2 nm.

[Thermoplastic Resin Composition]

The following is a description of the thermoplastic resin composition that is used in the present invention.

5 It is preferable to use a thermoplastic resin composition containing PBT or polyphenylene sulfide (PPS) as a main component. Further, it is necessary to match the coefficient of linear expansion of the thermoplastic resin composition to that of the aluminum alloy. Therefore, it
10 is important for the thermoplastic resin composition to contain a filler. First, it is necessary to use a fibrous filler, for example, glass fiber, carbon fiber, aramid fiber, and other high-strength fibers similar to these. However, if a fibrous filler is added singly, strong
15 directionality appears during injection molding, which is unfavorable depending upon the configuration. Therefore, it is preferable to use a thermoplastic resin composition containing a fibrous filler and a powder filler such as calcium carbonate, magnesium carbonate, silica, talc, clay,
20 glass, ground carbon fiber, ground aramid fiber, and other resin-filling inorganic fillers similar to them.

Further, injection molding is frequently used to obtain the desired composite from the viewpoint of productivity, cost, etc. In this case, the mold shrinkage
25 factor is also important. In conclusion, it is preferable that the mold shrinkage factor should be small. There is a method for minimizing the mold shrinkage factor, in which PBT or PPS is made to contain an amorphous polymer,

instead of using a thermoplastic resin composition consisting singly of PBT or PPS, which originally have a large mold shrinkage factor. More specifically, the thermoplastic resin composition may contain a
5 polycarbonate resin (hereinafter referred to as "PC"), an ABS resin (hereinafter referred to as "ABS"), a polyethylene terephthalate resin (hereinafter referred to as "PET"), or a polystyrene resin (hereinafter referred to as "PS").

10 The coefficient of linear expansion of the aluminum alloy is 2.2 to $2.5 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$. Therefore, if the average coefficient of lengthwise and crosswise linear expansion of the thermoplastic resin composition is 2 to $3 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$, the thermoplastic resin composition and the aluminum alloy
15 are approximately coincident with each other in terms of the coefficient of linear expansion. Even an average coefficient of lengthwise and crosswise linear expansion of 2 to $4 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$ is considered to be practically appropriate. In addition, the thermoplastic resin
20 composition should preferably have a mold shrinkage factor in the range of from 0.4 to 0.5% . It should be noted that the average coefficient of lengthwise and crosswise linear expansion is used for the thermoplastic resin composition for the following reason. The coefficient of linear
25 expansion is small in a direction in which the fibers of the resin composition mainly lie side-by-side with each other, but large in a direction perpendicular to the above-mentioned direction. Therefore, the average of the

coefficients of linear expansion in the two directions is used as an indication of the linear expansion coefficient of the resin composition.

[Integration of Aluminum Alloy and Resin Composition]

5 The most rational integrating process is as follows. An insert molding mold is prepared, and the aluminum alloy is inserted into the injection mold. Then, the thermoplastic resin composition is injected into the mold. It is preferable that when the molded article is removed
10 from the mold, the aluminum alloy and the thermoplastic resin composition should have already been bonded together into an integrated structure. However, in the ordinary injection molding, the injection mold has been adjusted to a temperature at which the resin is cooled to become
15 solidified, and the inserted metal piece is also at a temperature equal to or lower than the mold temperature. Therefore, the molten resin composition injected into the mold undesirably becomes solidified before entering the fine recesses formed on the aluminum alloy surface.

20 The following is common general technical knowledge to a person skilled in the technical field of injection molding. That is, it is not easy for the molten resin to enter pores of 5 μm or less in diameter open in the injection mold. It is almost impossible to make the molten
25 resin enter, at least, pores of 1 μm or less in diameter. Accordingly, it is impossible from the beginning to attain the desired integration at once by the ordinary insert molding. We confirmed the effectiveness of the present

invention by several conceivable methods. One of them is the commonest method of bonding using an adhesive. That is, an aluminum alloy and a resin molded material are prepared so that their surfaces to be bonded are completely
5 coincident with each other. For example, the two surfaces are formed into flat surfaces and bonded together with a solvent-free two-part adhesive, if possible.

The second is a method in which a metal material is previously covered with a resin film having an affinity
10 for PBT. This is inserted into an insert mold, and a resin composition is injected into the mold so as to bond to the metal material. For example, PBT dissolves in o-chlorophenol. Therefore, an organic solvent solution of PBT is prepared and put in a hermetically sealable
15 container. The above-described aluminum alloy is dipped in the solution. In this state, the pressure is reduced and raised repeatedly at short intervals, thereby allowing the solution to penetrate into the aluminum alloy surface thoroughly. Thereafter, the aluminum alloy is taken out of
20 the solution and dried by blowing nitrogen thereonto. With this process, an aluminum alloy coated with a thin PBT film can be produced.

The following is a method invented by the present inventors, on which we have applied for a patent
25 separately from the present application. That is, a paint or an ink is applied to a metal and hardened, and a PBT resin is injected onto the coated metal, thereby bonding them to each other. The main component of the paint or ink,

exclusive of the solvent used therein, may be a urethane curable, epoxy curable or modified alkyd curable material. For example, a two-part ink consisting essentially of a polyalcohol and a polyisocyanate, which is a urethane
5 curable ink, is printed on the above-described aluminum alloy and cured under curing conditions specified by the manufacturer of this ink.

By this curing process, about 50% of the curable component of the ink is cured. However, the rest of the
10 curable component remains unreacted. The ink takes several months or years to be cured completely. Probably, the uncured component reacts with the PBT resin when injected at a temperature not lower than the melting temperature thereof. As a result, the PBT resin and the print layer
15 bond to each other. In actuality, the bond strength varies to a considerable extent depending upon the kind of metal used. Therefore, it is necessary to select a suitable paint or ink by trial and error. There is a case where the adhesion between the paint or ink and the metal is weak.
20 In such a case, an appropriate primer may be needed.

The most direct method may be as follows. An aluminum alloy to be bonded by injection process is previously heated to a temperature close to the melting temperature of a PBT resin to be bonded. Then, the PBT
25 resin is injected onto the heated aluminum alloy. This method needs to cool the whole below the solidification temperature of the resin after the injection process and is therefore regarded as difficult to use from the

industrial point of view. However, the method is simple in theory.

The following is a method discovered by the present inventors. At the time of finely etching an aluminum alloy, it is dipped in an aqueous solution of at least one selected from the group consisting of hydrazine, ammonia, and a water-soluble amine compound, thereby treating the aluminum alloy so that it has a surface condition as defined in the present invention. After the dipping treatment, the aluminum alloy is rinsed with water and dried with air at a high temperature. Then, the aluminum alloy is inserted into an insert mold, and a PBT resin is injected into the mold. By doing so, injection bonding can be effected at the ordinary mold temperature. This method can ensure mass productivity, although it has not yet completely been clarified why the molten resin enters the fine recesses while remaining unsolidified (see WO 03/064150 A1).

Brief Description of the Drawings:

Fig. 1 is a photograph of a surface-treated aluminum alloy surface.

Fig. 2 shows the conditions of recesses observed from the photograph of Fig. 1 and the measured diameters of the recesses.

Fig. 3 shows a plate-shaped resin molded article.

Fig. 4 shows a test piece prepared by bonding the plate-shaped molded article and an aluminum alloy piece.

Fig. 5 is a sectional view of an injection mold for molding a test piece.

Fig. 6 shows a test piece molded by the injection molding apparatus shown in Fig. 5.

5 Fig. 7 is a sectional view of an injection mold having a heating device.

Fig. 8 shows a test piece molded by the injection mold shown in Fig. 7.

10 Fig. 9 is a scanning electron microscope photograph of a section of a bonded portion where an aluminum and a PBT resin are bonded to each other.

Fig. 10 is a scanning electron microscope photograph of the PBT resin removed from the section of the bonded portion shown in Fig. 9.

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Best Mode for Carrying Out the Invention:

Examples of the present invention will be described below in detail by way of experimental examples.

[Experimental Example 1]

20 A commercially available aluminum alloy plate A5052/H38 with a thickness of 1 mm was purchased. The aluminum alloy plate was cut into a rectangular piece of 100 mm by 25 mm. The aluminum alloy piece was dipped in 1 liter of ethanol for 10 minutes under application of
25 ultrasonic waves, and then dipped in 4 liters of tap water under stirring. Thereafter, the aluminum alloy piece was put into a plastic basket and washed with running tap water. Next, the aluminum alloy piece was dipped in a 2%

aqueous caustic soda solution for 2 minutes, followed by rinsing with ion-exchange water. Then, the aluminum alloy piece was dipped in a 1% aqueous hydrochloric acid solution for 1 minute to effect neutralization. Then, the
5 aluminum alloy piece was dip-washed in 4 liters of ion-exchange water, followed by rinsing with running ion-exchange water.

One liter of a 2% aqueous ammonia solution was prepared. A 1% aqueous caustic soda solution prepared
10 separately was dropped into the aqueous ammonia solution under stirring to adjust the pH to 11.0 at 50°C. The aluminum alloy treated as stated above was dipped in the aqueous solution for 2 minutes and then thoroughly washed with ion-exchange water. The aluminum alloy was dried with
15 hot air at 60°C for 20 minutes and then stored in dry air.

The aluminum alloy surface was observed by using a scanning electron microscope (SEM) "S-4700 (available from Hitachi, Ltd.)". A photograph of the aluminum alloy surface is shown in Fig. 1. Fig. 2 shows the conditions of
20 recesses on the aluminum alloy surface observed from the photograph of Fig. 1 and also shows the diameters of the recesses measured by drawing lines along the contours of the recesses. It was observed that there were 3 recesses of 0.03 to 0.1 μm in diameter and 15 to 20 recesses of
25 0.01 to 0.03 μm in diameter per 0.25 μm square area of the surface on the average. The densities of such recesses were substantially the same at different positions of observation.

The aluminum alloy surface was observed by using XPS (X-ray Photoelectron Spectroscopy). Only a slight amount of zero-valent aluminum element was detected even when the aluminum alloy was observed at a deepened angle. Most of the detected aluminum was + trivalent aluminum. XPS is said to be capable of analyzing the aluminum alloy to a depth of about 1 nm from the surface thereof. Therefore, the thickness of the aluminum oxide film was considered to be 1 to 2 nm.

10 [Experimental Example 2]

A thermoplastic resin composition was prepared by a twin-screw extruder and a pelletizer. The thermoplastic resin composition consisted essentially of 60% a polymer alloy containing 80% PBT and 20% PET, 20% glass fiber, and 20% glass powder filler. A rectangular molded article of 100 mm by 25 mm having a thickness of 3 mm was obtained by injection molding from a rectangular end. The coefficients of linear expansion in the lengthwise and crosswise directions were measured in the temperature range of from 0°C to 60°C. The average coefficient of linear expansion in the lengthwise direction was 2.1 to $2.3 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$. The average coefficient of linear expansion in the crosswise direction was 3.7 to $3.9 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$. The average of the coefficients of linear expansion in the lengthwise and crosswise directions was $3.0 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$.

[Experimental Example 3]

Injection molding was carried out by using as a raw material the thermoplastic resin composition pellets

prepared in Experimental Example 2, thereby obtaining a plate-shaped resin molded article 1 as shown in Fig. 3. As shown in Fig. 4, the resin molded article 1 and an aluminum alloy piece 2 were bonded together with an adhesive to obtain a test piece 3. Prior to the bonding process, a portion of the resin molded article 1 to be bonded was polished on a flat iron plate with calcium carbonate of 25 μm in average diameter and a small amount of water.

The resin molded article 1 was further polished with calcium carbonate of 5 μm in average diameter and a small amount of water and thoroughly washed with tap water under application of ultrasonic waves. After being placed in an air blast dryer at 50°C for 6 hours, the resin molded article 1 was stored in a desiccator for drying filled with concentrated sulfuric acid. The aluminum alloy piece 2 obtained in Experimental Example 1 was also stored in a desiccator for drying. The resin molded article 1 and the aluminum alloy piece 2 were stored in the respective desiccators for 1 week.

A two-part epoxy adhesive "Cemedine 1500 (registered trademark: available from Cemedine Co., Ltd.) was prepared as specified by the manufacturer. The adhesive was applied to the aluminum alloy, and the plate-shaped resin molded article was pressed against the adhesive-coated side of the aluminum alloy to bond them into an integrated article. Further, a weight of 15 kg was placed on the integrated article. This was allowed to stand for 2 days. Then, the

weight was removed, and the integrated article was allowed to stand for 1 week. Thereafter, both ends of the integrated article were set to a tensile testing machine to measure the tensile shear breaking strength. The
5 average of 10 measured values of the shear breaking strength of the bonded surface was 10.0 MPa (102 kgf per square centimeter).

[Reference Example 1]

A polished plate-shaped molded article made of a
10 resin composition was obtained in the same way as in Experimental Example 2 and stored in a desiccator for drying. Meanwhile, an aluminum alloy plate A5052/H38 with a thickness of 1 mm was cut into a rectangular piece of 100 mm by 25 mm. After being degreased and rinsed with
15 water in the same way as in Experimental Example 1, the aluminum alloy piece was dipped in a 20% aqueous caustic soda solution for 3 minutes and then thoroughly washed with ion-exchange water. Thereafter, the aluminum alloy piece was dried with an air blast at 50°C for 6 hours and
20 then stored in a desiccator for drying. The polished resin molded article and the aluminum alloy piece were stored in the respective desiccators for drying for 1 week.

One aluminum alloy piece was taken out from the desiccator to measure the surface roughness thereof.
25 Subsequently, the surface condition was analyzed by SEM and XPS. Regarding the surface roughness, 15 μ m was observed for a length of 2 mm. The SEM observation revealed that there were a few irregularities that were

regarded as pores or recesses having a diameter of not more than 0.1 μm , and there were many places where forming lines present on the aluminum alloy surface from the beginning (i.e. fine scratch lines cut on the aluminum alloy surface by a roll during manufacture of the aluminum plate) melted away, resulting in large gentle recesses or projections.

In the XPS observation, only a slight amount of zero-valent aluminum element was detected even when the aluminum alloy was observed at a deepened angle. Most of the detected aluminum was + trivalent aluminum. The magnitude of the detection peak of zero-valent aluminum was equal to or slightly larger than that in Experimental Example 1. XPS is said to be capable of analyzing the aluminum alloy to a depth of about 1 nm from the surface thereof. Therefore, the thickness of the aluminum oxide film was also considered to be about 1 nm.

This process may be summarized in comparison to Experimental Example 1 as follows: ① the surface roughness is similarly large; ② the surface area is small; and ③ the thickness of the oxide film is equal to or slightly smaller than that in Experimental Example 1. The remaining aluminum alloy pieces were taken out from the desiccator and bonded to resin molded articles, respectively, with an adhesive to form integrated articles in the same way as in Experimental Example 3. After a while, tensile testing was performed on the integrated articles. Ten integrated articles were tested. The

average of 10 measured values of the shear breaking strength of the bonded surface was 7.6 MPa (78 kgf per square centimeter). This was lower than the value in Experimental Example 3.

5 [Reference Example 2]

A polished plate-shaped molded article made of a resin composition was obtained in the same way as in Experimental Example 3 and stored in a desiccator for drying. Meanwhile, an aluminum alloy plate A5052/H38 with
10 a thickness of 1 mm was cut into a rectangular piece of 100 mm by 25 mm and subjected to an aluminum anodizing process. That is, the aluminum alloy piece was dipped in a 20% aqueous solution of a commercially available aluminum degreasing material for 10 minutes, following by rinsing
15 with water. Subsequently, the aluminum alloy piece was dipped in a 20% aqueous caustic soda solution at 90°C for 20 seconds, followed by rinsing with water. Then, the aluminum alloy piece was dipped in a mixed acid liquid of sulfuric acid and phosphoric acid at 100°C for 2 minutes,
20 followed by rinsing with water.

Subsequently, an electrode was bonded to an end of the aluminum alloy, and anodizing was performed for 20 minutes under application of a voltage of 15 v in a 40% aqueous sulfuric acid solution kept at 20°C, followed by
25 rinsing with running ion-exchange water. The anodized aluminum alloy piece was dried with an air blast at 50°C for 6 hours and then stored in a desiccator for drying. The polished resin molded article and the aluminum alloy

piece were stored in the respective desiccators for drying for 1 week.

One aluminum alloy piece was taken out from the desiccator to measure the surface roughness thereof.

5 Subsequently, the surface condition was analyzed by SEM and XPS. Regarding the surface roughness, 13 μm was observed for a length of 2 mm. The SEM observation revealed that the aluminum alloy surface was closely crowded with irregularities regarded as pores and recesses
10 or projections having a diameter of 0.05 to 0.1 μm . That is, the observed aluminum alloy surface was the same as an anodized aluminum surface before sealing. In the XPS observation, no zero-valent aluminum element was detected even when the aluminum alloy was observed at a deepened
15 angle. The detected aluminum was + trivalent aluminum.

There was no metallic aluminum within the XPS reachable range. Thus, the experimental result agreed with the conventional knowledge. This process may be summarized in comparison to Experimental Example 1 as follows: ① the
20 surface roughness is similarly large; ② the surface area is not remarkably large, but the pores are fine and deep, with an inner diameter of 0.05 μm ; and ③ the thickness of the oxide film is several μm . The thickness of the thinnest film portion (pore bottom) could not be measured
25 and hence unknown.

The remaining aluminum alloy pieces were taken out from the desiccator and bonded to resin molded articles, respectively, with an adhesive to form integrated articles

in the same way as in Experimental Example 3. After a while, tensile testing was performed on the integrated articles. Ten integrated articles were tested. The average of 10 measured values of the shear breaking strength of the bonded surface was 90 kgf per square centimeter. This was equal to or slightly lower than the value in Experimental Example 3. The present inventors considered that because the recesses or projections on the aluminum alloy surface were excessively fine, the adhesive could not enter such fine recesses. Therefore, the shear breaking strength weakened undesirably despite the enlarged surface area.

[Experimental Example 4]

The aluminum alloy pieces in Experimental Example 1 were transferred to a desiccator for drying. Meanwhile, 5 g of PBT pellets "Tufpet N1000 (available from Mitsubishi Rayon Co., Ltd.) was put into a beaker and dissolved in 200 g of orthochlorophenol added thereto under stirring with a stirrer and a magnetic stirrer. The beaker was put into a large-sized desiccator filled with nitrogen. Further, 5 aluminum alloy pieces were dipped in the solution in the beaker by being stood against the wall of the beaker in such a manner as not to overlap each other.

The pressure in the desiccator was reduced to 500 mmHg and kept at this level for 1 minute. Then, nitrogen was introduced into the desiccator to return the pressure therein to the ordinary pressure (760 mmHg).

After 1 minute, the pressure in the desiccator was reduced again. This pressure reducing process was repeated 10 times. Thereafter, the pressure in the desiccator was returned to the ordinary pressure. After 1 hour, the
5 desiccator was opened, and the aluminum alloy pieces were taken out from it while draining off the liquid, and then dried for 2 hours. Subsequently, the aluminum alloy pieces were placed in an air blast dryer at 50°C for 48 hours. Then, the aluminum alloy pieces were transferred to a
10 desiccator and placed under a reduced pressure of 10 mmHg for 1 hour. Thereafter, the aluminum alloy pieces were placed under a reduced pressure of 1 mmHg for 1 hour and then under a reduced pressure of 0.01 mmHg for 24 hours, thereby allowing the solvent to evaporate.

15 An aluminum alloy piece 5 coated with a thin PBT film thus obtained was inserted into an insert mold 10 as shown in Fig. 5, which had been heated to 110°C, and the thermoplastic resin composition obtained in Experimental Example 2 was injected into the mold 10 at an injection
20 temperature of 280°C. After 40 seconds, the mold was opened. Thus, an integrated molded article was obtained. After two days, the tensile shear breaking strength of the integrated molded article was measured with a tensile testing machine. Five integrated molded articles were
25 tested. The average of 5 measured values of the shear breaking strength of the bonded surface was 3.0 MPa (31 kgf per square centimeter).
[Experimental Example 5]

On the aluminum alloy piece in Experimental Example 1, a two-part urethane curing type ink "VIC White (available from Seiko Advance Ltd.)" was printed by using a 270-mesh screen printing plate and baked at 100°C for 1 hour in a hot-air dryer. Then, the aluminum alloy piece was inserted into the insert mold 10 shown in Fig. 5, which had been heated to 100°C, and the thermoplastic resin composition obtained in Experimental Example 2 was injected into the mold 10 at an injection temperature of 280°C. After 40 seconds, the insert mold 10 was opened. Thus, an integrated molded article 15 as shown in Fig. 6 was obtained. After 2 days, the tensile shear breaking strength of the integrated molded article 15 was measured with a tensile testing machine. Ten integrated molded articles were tested. The average of 10 measured values of the shear breaking strength of the bonded surface was 12 kgf per square centimeter.

[Experimental Example 6]

An aluminum alloy plate A5052/H38 with a thickness of 1 mm was cut into a rectangular piece of 100 mm by 25 mm. Further, a groove having a width of 0.5 mm and a depth of 0.7 mm was cut longitudinally in the center of the aluminum alloy piece with a length of 5 mm left uncut at an end thereof. Ten aluminum alloy pieces prepared in this way were treated in the same way as in Experimental Example 1. The treated aluminum alloy pieces were transferred to a desiccator for drying and allowed to stand for 1 week.

Meanwhile, an insert injection mold 23 as shown in Fig. 7 was made. In Fig. 7, a movable retainer plate 16 has a part (shaded part) made of a Bakelite material 17. The movable retainer plate 16 is provided with electrodes 18 for supplying electric power for heating, a through-opening (not shown) for suction-holding an insert material, a groove (not shown) for fitting a thermocouple, etc. A resin is injected into a stationary retainer plate 19. The injection mold 23 was heated to 110°C in advance.

One aluminum alloy piece 20 was taken out from the desiccator, and a superfine thermocouple (not shown) available from Sukegawa Electric Co., Ltd. was fitted into the groove thereof and locally fixed with a small amount of epoxy adhesive. The thermocouple is an alumel-chromel thermocouple inserted into a protecting tube of SUS having an outer diameter of 0.5 mm. In addition, a surface of the aluminum alloy piece 20 that was to be brought into contact with the electrodes 18 of the injection mold 23 was polished with sandpaper to facilitate the passage of electric current. The aluminum alloy piece 20 with the thermocouple was inserted into the movable retainer plate 16 and secured by using a vacuum. Then, the injection mold 23 was closed (as shown in the sectional view of Fig. 7).

The aluminum alloy piece 20 was supplied with an electric current while the temperature was being checked with a thermometer connected to the thermocouple (alternatively, the aluminum alloy piece 20 may be heated by heating a heating wire 21 disposed as shown in Fig. 7).

When the aluminum alloy piece 20 was going to exceed 200°C, the heating power supply was cut off. At the same time, the thermoplastic resin composition 22 obtained in Experimental Example 2 was injected. 120 seconds after the
5 injection, the injection mold 15 was opened, and a molded article 25 as shown in Fig. 8 was removed from the mold 15. The adhesive was removed with a knife to detach the thermocouple from the molded article. Thereafter, the molded article was handled in the same way as in
10 Experimental Example 5. Finally, the tensile shear breaking strength of the molded article was measured. Ten molded articles were tested. The average of 10 measured values of the shear breaking strength of the bonded surface was 2.3 MPa (23 kgf per square centimeter).

15 [Experimental Example 7]

An aluminum alloy plate A5052/H38 with a thickness of 1 mm was cut into a rectangular piece of 100 mm by 25 mm. The aluminum alloy piece was dipped in 1 liter of ethanol for 10 minutes under application of ultrasonic
20 waves, and then dipped in 4 liters of tap water under stirring. Thereafter, the aluminum alloy piece was put into a plastic basket and washed with running tap water. Next, the aluminum alloy piece was dipped in a 2% aqueous caustic soda solution for 2 minutes, followed by rinsing
25 with ion-exchange water. Then, the aluminum alloy piece was dipped in a 1% aqueous hydrochloric acid solution for 1 minute to effect neutralization. Then, the aluminum alloy piece was dip-washed in 4 liters of ion-exchange

water, followed by rinsing with running ion-exchange water.

One liter of a 5% aqueous hydrazine monohydrate solution was prepared and heated to 50°C. The pH of the aqueous solution was 11.2. The foregoing aluminum alloy
5 piece was dipped in the aqueous solution for 2 minutes and then thoroughly washed with ion-exchange water. The aluminum alloy piece was dried with hot air at 60°C for 20 minutes and then stored in dry air.

The same mold as in Experimental Example 4 was used.
10 With the mold temperature kept at 100°C, the above-described aluminum alloy piece was inserted into the mold, and the thermoplastic resin composition shown in Experimental Example 2 was injected into the mold at an injection temperature of 280°C. After 40 seconds, the mold
15 was opened to obtain a molded article. After 2 days, the tensile shear breaking strength of the molded article was measured. It exhibited a very high value, i.e. 10.8 MPa (110 kgf per square centimeter).

The integrated article thus obtained was cut and
20 polished to prepare a sample that enabled a section of the bonded portion to be observed with an SEM. An SEM photograph of the section of the bonded portion is shown in Fig. 9. It will be understood from the photograph that the PBT resin entered every corner of the recesses of the
25 aluminum alloy. The photograph of Fig. 9 shows that large pores having a diameter of about 0.3 to 0.8 μm are formed, and small pores are formed in the bottom or side surfaces of the large pores in the shape of inlets. The PBT is

fixed in such a manner as to fill the large and small pores.

By way of precaution, an aluminum alloy piece that had been subjected to the shear breaking strength test and
5 that had dots of resin attached to the surface thereof was put in 5 liters of a 5% aqueous hydrochloric acid solution and allowed to stand for 1 week. As a result, the aluminum alloy piece was dissolved. The solution was filtered, and the residue was rinsed with water and dried. Then, it was
10 observed with an SEM. An SEM photograph thereof is shown in Fig. 10. The PBT in the recesses were released and semi-dissolved in the shape of spheres by the acid. The diameter of the spheres was from 0.02 to 0.1 μm . The size of the spheres was closely coincident with the size of the
15 recesses formed on the aluminum alloy surface.

[Experimental Example 8]

The integrated article obtained in Experimental Example 7 was subjected to colored aluminum anodizing treatment. That is, the integrated article was dipped in a
20 20% aqueous solution of a commercially available aluminum degreasing agent for 10 minutes, followed by rinsing with water. Subsequently, the integrated article was dipped in a 20% aqueous caustic soda solution at 60°C for 40 seconds, followed by rinsing with water. Then, the integrated
25 article was dipped in a mixed acid liquid of sulfuric acid and phosphoric acid at 80°C for 2 minutes, followed by rinsing with water. Subsequently, an electrode was bonded to an end of the aluminum alloy, and anodizing was

performed for 20 minutes under application of a voltage of 15 v in a 40% aqueous sulfuric acid solution kept at 20°C, followed by rinsing with running ion-exchange water. Further, the integrated article was dipped for 3 minutes
5 in water having a dye dissolved therein and kept at 90°C to effect dyeing, followed by rinsing with water. Then, the integrated article was dipped in a 30% aqueous phosphoric acid solution at 100°C for 5 minutes to effect sealing, followed by rinsing with water. Then, the
10 integrated article was dried with hot air at 70°C for 1 hour.

In this experiment, the aluminum anodizing treatment was performed at a slightly reduced temperature in comparison to the ordinary aluminum anodizing treatment to
15 minimize the damage to the resin, and the dipping time was made longer than in the ordinary aluminum anodizing treatment in compensation for the reduction in temperature. This seemed to be a successful procedure. That is, the aluminum alloy surface was the same as the ordinary
20 colored anodized aluminum surface. After the aluminum anodizing treatment, the tensile shear breaking strength of the integrated article was measured. Three integrated articles were tested. The average of 3 measured values of the shear breaking strength of the bonded surface was
25 9.0 MPa (92 kgf per square centimeter). Therefore, we judged that the colored aluminum anodizing treatment did not cause much damage to the bonded surface or the resin.

This experiment reveals that aluminum anodizing

treatment can be performed even after the integrated article has been formed by carrying out the present invention, and it is possible to ensure the same weather resistance as obtained with the conventional procedure for any molded article wherein an aluminum material

5 constitutes the surface layer.

[Experimental Example 9]

An experiment was performed on 10 aluminum alloy pieces obtained in Experimental Example 1 (samples

10 obtained by a caustic treatment process seeming as if it were finely adjusted eventually), 10 aluminum alloy pieces obtained by Reference Example 1 (samples obtained by a simple caustic treatment process), and 10 aluminum alloy pieces obtained by Reference Example 2 (samples obtained

15 by a treatment process using anodizing and regarded as providing fine pores and the largest surface area). These aluminum alloy pieces were laid side-by-side in a dark room with an open window, that is, in a place where neither light nor rain could enter, but communication with

20 the outside air was available. The aluminum alloy pieces were allowed to stand in the dark room.

At the beginning, the aluminum alloy pieces were dried in a desiccator for 2 days. Then, the weight of each aluminum alloy piece was measured. After 1 year, each

25 aluminum alloy piece was dried in a desiccator for 2 days, and the weight thereof was measured again. All the three different groups of aluminum alloy pieces weighed around 6.7 g at the beginning and had a similar weight increase

of 0.003 g. We considered that the aluminum alloy surface obtained in Experimental Example 1 would not be used as an exterior surface as it was.

We considered that when used as an exterior surface,
5 the aluminum alloy surface would be anodized as in
Experimental Example 8, or the aluminum alloy surface
obtained in Experimental Example 1 would be painted.
Further, we considered that when used as an interior
surface, the aluminum alloy surface would not be painted.
10 This experiment assumes a case where the aluminum alloy
surface is not painted. Therefore, we carried out the
experiment on the assumption that the aluminum alloy
surface would be exposed to air, considered to be the same
as the outside air, but not exposed to sunshine nor water.
15 Measurements made in the middle of the experiment, i.e.
when 1 year had elapsed, revealed that the measurement
results were not different from those of the anodized
aluminum products.

20 Industrial Applicability:

The present invention is industrially applicable in
the fields of various electronic devices for mobile
applications, home electrical products, medical devices,
automotive bodies, vehicle-mounted products, construction
25 material parts, structural parts of various other machines,
various parts for interior and exterior applications, and
so forth.